The W center in self-implanted silicon is the self-interstitial cluster I_3

Giorgia M. Lopez and Vincenzo Fiorentini
INFM and Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy
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We identify the W center in self-implanted crystalline Si with the three-membered self-interstitial cluster I_3 on the basis of first-principles density-functional-theory calculations matching all the known experimental signatures of the center (emission energy, extrinsic energy levels, activation energy and dissociation energy, local vibrational structure, and symmetry).

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Self-implanted Si is relevant to the pre-amorphization processes used at various stages of device fabrication, and as a model environment for the study of anomalous interstitial-driven impurity diffusion. A prominent defect in self-implanted Si is the so-called W center, which has been known and studied intensely for a long time [1,2], but not firmly identified so far, although generally accepted to originate from the clustering of excess interstitial Si atoms [3–5]. By means of first-principles density-functional calculations, we provide a conclusive identification of the W center with the I_3 three-membered self-interstitial cluster. Remarkably for a difficult enterprise such as the identification of defects in crystals, our results match all the experimental signatures available for this center, and confirm the relevance of ab initio calculations for the physics of defects and impurities in crystals.

Recent experimental studies [3,4], performed with a variety of combined techniques, including variable-dose implant, rapid thermal annealing (RTA), deep level transient spectroscopy (DLTS), and photoluminescence (PL), have firmly identified several experimental signatures of the W defect. By carefully cross-referencing a number of n-type samples with different implant and RTA histories, Libertino *et al.* [3] identified a low-dose implant regime in which the extended {311} defects – a common product of self-interstitial aggregation – do not form: small, nearly point-like entities are active instead. They suggested that the W photoluminescence line, a typical emission at 1.018 eV in self-implanted Si, is indeed the main signature of these centers. A second signature identified as strongly correlated with this emission, is a pair of extrinsic levels determined by DLTS at about 0.35 and 0.6 eV above the valence edge. The third signature brought forth by the analysis of the pertaining DLTS signals under thermal treatment is the activation energy of around 2.3 eV needed to cause the essentially concurrent disappearance of these two levels upon RTA. In addition, the appearance of the W band is itself thermally activated, with a characteristic energy of about 0.85 eV [4,6] – the fourth signature of W. A fifth group of signatures stems from the vibronic structure of which the W emission is the zero-phonon line; this structure has been known for some time [2] to include main peaks at 17 meV and 40 meV, and a local vibrational mode at 70 meV [2]. The symmetry of the center identified via the stress response of the vibronic structure is at least C_{3v}. Finally, several indirect hints led many authors (see e.g. [3] for a summary) to postulate the most likely size of the cluster responsible for these signatures to be n=3, with a high-symmetry compact structure, as opposed to the non-compact I_4 and asymmetric I_2 clusters found in recent calculations [7–9].

In the following, we give evidence that the I_3 Si tri-interstitial is to be identified with the W center, as its properties explain all the mentioned experimental signatures. Our conclusion is based on a series of ab initio calculations on self-interstitial clusters in c-Si (full details are reported elsewhere [7]), performed at the first-principles level within density-functional theory in the generalized gradient approximation (GGA) [10], and the ultrasoft pseudopotential-plane wave repeated-supercell approach using the Vienna Ab-initio Simulation Package code [11]. We report data obtained with 32- and 64-atom supercells (the results are in fact quite insensitive to cell size), multiprojector ultrasoft pseudopotentials [11] (with two s, two p, and one d projectors, r_c=1.31 Å), a plane wave cutoff of 151 eV, and a 444 k-space summation mesh (this yields 32 k-points in the Brillouin zone for C_1, i.e. no, imposed symmetry; in occasional test we used 666 and 888 meshes, with 108 and 256 k-points respectively). Atomic geometries are relaxed until all force components are below 0.01 eV/Å. The theoretical lattice constant $a_{\rm Si}$=5.461 Å is used throughout. The formation energies and extrinsic levels are obtained in the usual way (see e.g. Refs. [12] and [13]), including multipole corrections for charged states [14].

We obtained the equilibrium structure of the I_3 cluster by relaxation of a supercell containing an I_2 di-interstitial cluster [7–9] and a single interstitial I_1 in the adjacent tetrahedral site, both in the neutral state. The interstitial binds spontaneously to I_2, producing the I_3 structure depicted in Fig. 1. This structure agrees well with recent tight-binding [8] and ab initio results [15], although not with others [16] (incidentally, the properties of the n=3 cluster studied in [16] do not correlate well with those of the W center). The interatomic distances between the

four atoms (dark grey in Fig. 1) involved in the local structure of I_3 are essentially identical, 2.488±0.002 Å or 1.054 times the calculated Si-Si bond length of 2.365 Å. All bonds are oriented along (110)-equivalent directions, hence the four atoms form a perfect tetrahedron with edges aligned with the cubic (110) axes, and whose centerpoint is at a lattice site. The local symmetry of the cluster is therefore T_d. This agrees with the response of the zero-phonon W line to applied stress and its dependence on the electric field direction. The symmetry of the cluster, we point out, is obtained spontaneously in the simulated assembly of I_2 and tetrahedral I_1 *without* imposing any initial symmetry.

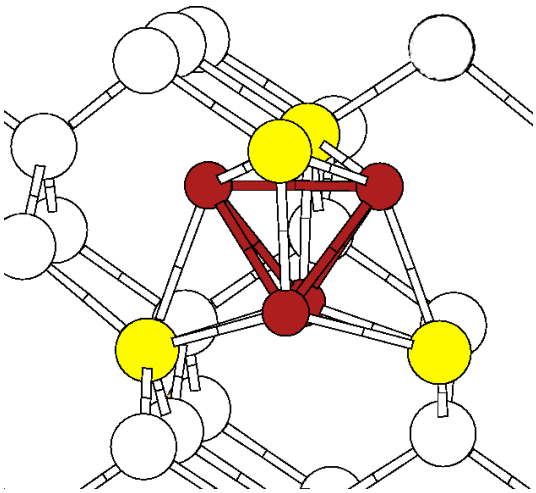

FIG. 1. View of the structure of the I_3 self-interstitial cluster in *c*-Si. Cluster atoms are dark grey, while their first bulk-like neighbors, involved in the 70-meV local vibrational mode (see text), are light grey. Bulk atoms are white.

Studying the energies of different charge states of the defect, we determined the extrinsic levels. I_3 possesses two extrinsic thermal charging levels in the gap, namely $\epsilon(++/+)$=0.35 eV + E_v and $\epsilon(+/0)$=0.8 eV + E_v, with E_v the valence band top. These values are close to the experimental values of 0.35 eV and 0.6 eV. Since the samples of interest here are *n*-type, these levels are filled and DLTS-detectable. Since a supersaturation of Si interstitials in *c*-Si produces moderate *n*-type conditions [7], this conclusion will hold even in as-implanted intrinsic samples. The DLTS signatures of the W center are thus reproduced by the I_3 cluster.

To interpret the thermal evolution of these levels, we assume that their disappearance under thermal treatment is due to the evaporation of the cluster into single interstitials. For the *n*-type Fermi level of relevance here, we find that all the interstitial complexes I_1, I_2, and I_3 are in their neutral state. We then estimate the cost of splitting I_3 into well-separated neutral I_2 and (neutral dumbbell) I_1 by direct comparison of calculated total energies : this cost is 2.38 eV, matching very closely the deactivation energies, 2.28 eV and 2.36 eV (estimated experimental error $\simeq$ 15%), of the observed DLTS peaks, confirming our previous attribution of those peaks to the I_3 extrinsic levels.

After splitting an I_3 into an I_2 and an I_1, one may still have electrically active levels present, since both the latter centers have extrinsic levels [7] in the 0.25-0.35 eV and 0.6-0.8 eV range. The observation of those levels is however preempted by two facts: *a)* I_2 splits into two I_1's with an energy cost of 1.5 eV, hence the thermal treatment dissolving the I_3's also gets rid of any I_2's; *b)* an I_3-cracking thermal process should presumably cause the remaining I_1's (also electrically active [7]) to evaporate off the sample, both because they are quite rapidly diffusing [17] neutral dumbbells, and because they have no effective capture centers, such as vacancies, available in sufficient concentration.

Of course the main signature of the center at issue is the W emission itself. The relevant emission energy is 1.02 eV; since the material is *n*-type, the transition is probably bound-to-free. Since the gap of Si is about 1.1 eV at the relevant temperature, the involved level lays ∼80 meV below the conduction edge. This does not imply, however, a delocalized state as in shallow impurities, the very existence of a sharp zero-phonon line in an indirect gap material indicating a localized character. We find the 0/– level of I_3 at 1.10 eV above the valence (k-points convergence was checked to better than ±10 meV up to the (888) mesh; no change was observed between 32-, 64- and 265-atom cells). This is clearly a very good candidate for the initial state of the emission: its energy is quite close to the observed transition and, since emission is involved, the Franck-Condon principle dictates that the emission energy coincides with the charging level in this case. In addition, this state is empty in thermal equilibrium, and can thus receive the photoexcited electrons thermalizing down from the upper conduction states. We find that the state is orbitally non-degenerate, in agreement with the analysis of the phonon replicas and with the absence of pseudo–Jahn-Teller distortions [2]. To give a proper estimate of the position of the state with respect to the conduction band, we calculated the fundamental gap of Si using the expression, exact in the $N \to \infty$ limit [18],

$$E_{\rm gap} = E_{\rm tot}(N+1) - 2E_{\rm tot}(N) + E_{\rm tot}(N-1), \qquad (1)$$

using an undefected 64-atom supercell with N, N+1, and N–1 electrons. The gap energy thus obtained is 1.13 eV, which gives a 30 meV binding energy. The satifactory agreement with experiment further confirms our identification [19].

We now consider the activation barrier for the *creation* of the center, which was quantified in 0.85 eV in Refs. [4,6]. The simplest interpretation is that the diffusive motion of the interstitials must be activated to achieve

clustering. It is natural to presume that at least two processes are to be activated to form I_3: the diffusion of I_1's towards each other to form I_2, and the diffusion of I_1 towards I_2 to form I_3. We estimated (see also [17]) a minimum energy barrier for the dumbbell-to-dumbbell diffusion of 0.2 eV via a tetrahedral site and 0.18 eV via an hexagonal site. This is much lower that the experimental activation energy. We then hypothesized that I_1 be subject to a local repulsion by its companion center (another I_1 or the I_2), effectively increasing its diffusion barrier. To check this idea we compare the energy of a dumbbell self-interstitial and a tetrahedral I_1 in the same cell in adjacent sites – i.e. the last saddle-point configuration before I_2 formation [7] – with the sum of the energies of an isolated dumbbell I_1 plus an isolated tetrahedral I_1. The difference is an estimate of the local repulsion (if any) between single interstitials. We then calculate the same difference for I_2 and tetrahedral I_1 in the same cell, and isolated I_2 plus isolated tetrahedral I_1. Again, the difference is an estimate of the local repulsion (if any) between I_1 and I_2. In both cases we obtain an effective repulsion, of 0.64 eV in the first case, and 0.53 eV in the second case (errors due to finite-size relaxation effects are at least one order of magnitude smaller [7]). Therefore, an effective repulsion acts locally between the precursors of I_3 (I_1's and I_2) The largest of these two repulsion energies, added to the normal diffusion barrier, provides an estimate of the maximum effective barrier. The result is 0.84 eV, in close agreement with the experimental estimate of 0.85 eV. Thus, an effective local repulsion between the component centers of the I_3 cluster explains quantitatively the activation-energy signature of the W-band center.

We now analyze the vibrational modes of the center. The zero-phonon W line splits under (110)- and (111)-oriented, but not under (100)-oriented stresses [2]. This is quite compatible with the symmetry and orientation of the I_3 complex, a tetrahedron with (111)-oriented axes and (110)-oriented bonds. The analysis of the phonon replicas of Ref. [2] suggests a dominance of couplings to the Si bulk phonon continuum. The main features in the replica spectrum [2] are broad structures associated with vibrational energies of 17 meV and 40 meV. Further, sharper but much weaker lines exist in the optical-mode energy region. An additional peak at 70 meV below the zero-phonon line appears to involve [2] a local vibrational mode (the highest vibrational energy in Si bulk is $\hbar\omega_{\rm TO}^{\rm Si}(\Gamma)$=64 meV).

To identify possible local modes, we estimated the vibrational frequency of selected normal modes of the cluster via the frozen-phonon method [20] in which a given displacement pattern is frozen into the lattice, and the force/displacement ratio for the atoms involved yields the mode's harmonic force constant. The calculated Si LO-TO mode energy at Γ of 62.4 meV, –2.5% from experiment [21] sets a reliability reference. The internal vibrational modes of the cluster, i.e. those involving the four atoms of the cluster, are found to have energies in the range 35–45 meV. The modes considered include most of the typical modes of a tetrahedron (breathing, twist, pinch, etc.) schematized e.g. in Fig. 2.5 of Ref. [22]. A detailed discussion will be presented elsewhere. The relatively low frequencies of the internal modes are unsurprising if we consider the weaker bonding within the cluster compared to the bulk: this is apparent from the (110)-plane slice of the charge density [23] through one of the internal cluster bonds of neutral I_3 in Fig. 2. The "translational" mode of I_3, in which the whole cluster moves with respect to the crystal, and which would have zero frequency for the cluster in free space, has a low energy of 19 meV. This is expected since the cluster is also quite weakly bound to the surrounding bulk (Fig. 2).

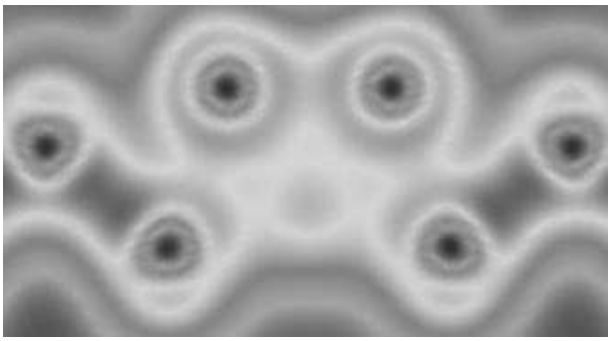

FIG. 2. Charge density contour plot in a (110) plane passing through one of the internal bonds of the I_3 tetrahedron. Two of the cluster atoms are visible (center top). The amount of bonding charge between the cluster atoms, and towards the bulk atoms, appears modest when compared to bulk-like bonds.

Their highest frequency being less than 45 meV, none of the internal vibrations can explain the 70-meV local mode [2]. Remarkably, indeed, it turns out that the local mode is not a proper cluster mode: after some search we identified it with the vibration of each of the four cluster-adjacent atoms (light grey in Fig. 1) in the (111) planes parallel to the corresponding triangular face of the tetrahedral cluster. The mode energy of 71.4 meV matches well the observed 70 meV shift of the local-mode replica. Its isotropic character (four equivalent atoms are involved, near each cluster face), and its strong expected dependence on (110)- and (111)-oriented strains also agree with the observed properties of the local-mode replica [2]. The mode clearly derives from a TO wave impinging on the I_3 cluster from a (111) direction – pictorially, a "breaker-on-the-shoal" effect.

As for the prominent 17 meV and 40 meV replica structures, they can be interpreted as suggested [2] as the interaction signature of I_3 with the bulk phonon continuum, with some contribution, we add, of the internal

modes of the cluster. The phonon dispersion and density of states of Si [24] suggest that the modes involved in the 5-meV–wide structure at about 17 meV are mainly the zone-border modes at the K and X points (e.g. the Σ_3 TA mode at K, e.g., has the correct 18 meV energy). The "translation" mode of the cluster mentioned earlier, with its energy of 19 meV, is also expected to be involved in this replica. For the 40-meV feature, the phonon density-of-states weight comes mainly from the LA modes along the Λ line, topping with the 46-meV L_2 mode at L. As mentioned, the 35–45 meV internal modes of the clusters t are also most likely to be involved in the 40-meV replica, superposed on the bulk continuum, and contributing to its substantial (10 meV) linewidth. With these attributions of vibrational signatures, in particular of the local mode, we conclude our identification of the I_3 cluster with the *W* center.

In summary, ab initio calculations of emission, activation, and dissociation energy, extrinsic levels, and vibrational modes explain all the known experimental features associated with the *W* band in self-implanted Si (PL emission, DLTS signatures of electronic levels, RTA behavior, phonon replicas in the PL spectra) as being due to the tri-interstitial cluster I_3. The W center remains thus unambiguously identified with the I_3 self-interstitial cluster.

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